VI. Typical Examples and Statistical Physics of Some real systems

Objectives: See how canonical ensemble approach works

Gain physical sense on real physical systems

Contrast canonical with microcanonical ensemble

"Two-level Systems"

Relevant physical systems:
- Defects in Solids
- Amorphous solids at low temperatures
- Paramagnetism in Solids
- Collection of Nuclear Spins

Canonical Ensemble

$Z(T,V,N)$, z, $\langle E \rangle$, C_V, F, S

Microcanonical Ensemble

$W(E,N,V)$, S, T, C_V

But physics is physics!

Thus, the same physics results.

VI. Examples

A. Two-level Systems

System: A collection of N distinguishable independent particles, each of which can exist in one of two states given by

$\epsilon_u = +\frac{\epsilon}{2}$

$\epsilon_l = -\frac{\epsilon}{2}$

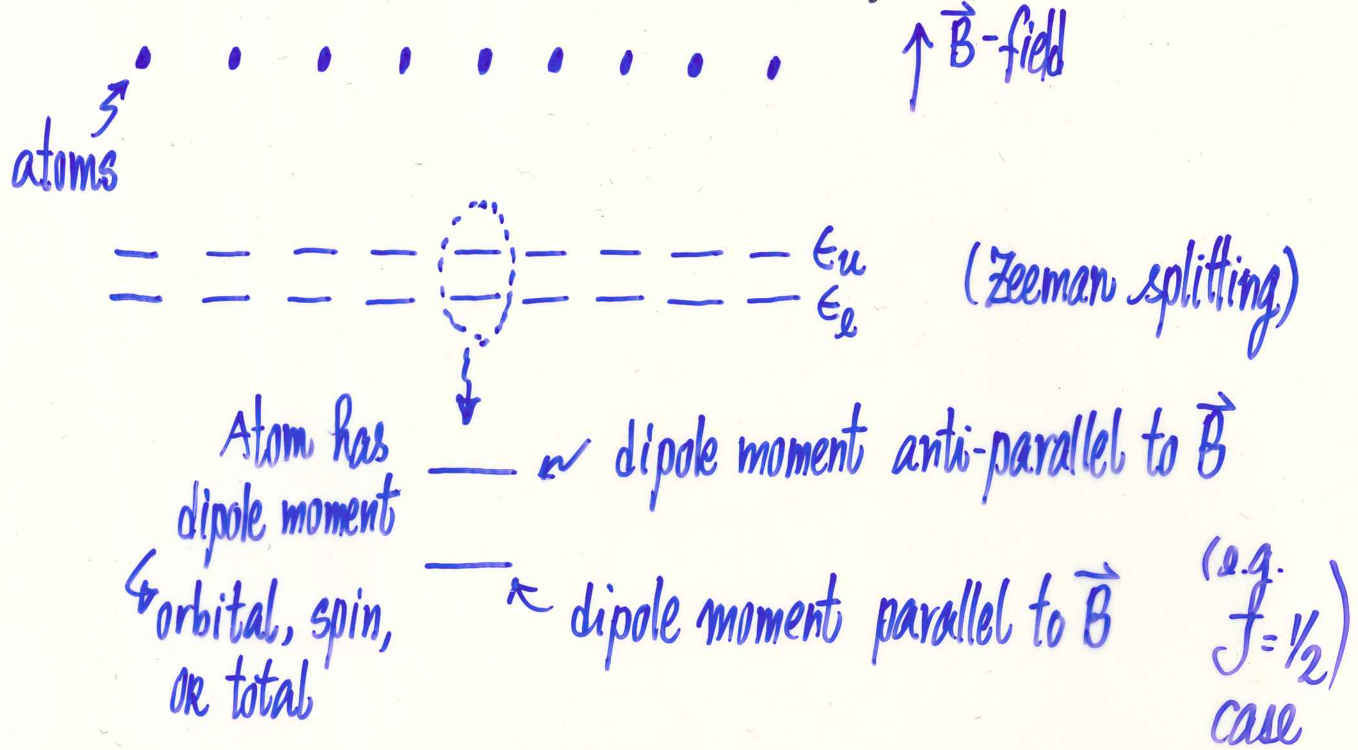
energy	(degeneracy)
ϵ_u	1
ϵ_l	1

two single-particle states (same for all particles)

Distinguishable: In many stat. mech. problems, even the particles are identical, they may still be distinguishable (e.g. by their locations)

Independent: One particle is not affecting another particle [non-interacting]

• A possible physical scenario: paramagnetism



- In this case, while atoms are identical, they can be distinguished by their locations
- Since atoms are identical, they have the same ε_ℓ and ε_u.

Strategy

• Independent particles — using this fact to simplify the calculation of Z to the calculation of z (one-particle partition function)
i.e., Z can be factorized

• Distinguishable — Nice! Don't need to worry about factor $\frac{1}{N!}$, etc.

(a) Work out $Z(T,V,N)$

By definition, $$Z = \sum_{\substack{\text{all } N\text{-particle}\\ \text{states } i}} e^{-\beta E_i}$$ (completely general)

[General! OK for interacting N-particle systems!]

Here, pay attention to what "independent" and "distinguishable" lead to.

• What is a state of the system?

Particles: 1 2 3 4 . . N

upper (u) or lower (ℓ) energy : $\underbrace{u \quad \ell \quad \ell \quad u \quad \cdots \quad \ell}$

a string $\{u, \ell, \ell, u, \cdots, \ell\}$ specifies a state

or (equivalently)

a string $\{\varepsilon_{u1}, \varepsilon_{\ell 2}, \varepsilon_{\ell 3}, \varepsilon_{u4}, \cdots \varepsilon_{\ell N}\}$ specifies the same state

upper energy of particle # 1 — lower energy of particle #3

ε_{u1} —— ε_{u3} ——

$\varepsilon_{\ell 1}$ —— $\varepsilon_{\ell 3}$ ——

may be different (generally)

For a given string (given state)

e.g. $\{\varepsilon_{u1}, \varepsilon_{\ell 2}, \varepsilon_{\ell 3}, \varepsilon_{u4}, \cdots ; \varepsilon_{\ell N}\}$

the energy E is

$$E = \varepsilon_{u1} + \varepsilon_{\ell 2} + \varepsilon_{\ell 3} + \varepsilon_{u4} + \cdots + \varepsilon_{\ell N}$$

- <u>Sum over all N-particle states</u>
  - Sum over <u>all strings</u>

    $\{\alpha_1, \alpha_2, \alpha_3, \alpha_4 \cdots, \alpha_N\}$

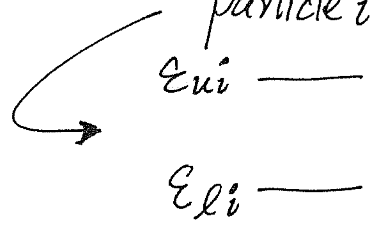
    with $\alpha_i = \ell, u$ (How many of them?)

  - OR equivalently sum over all strings[+]

    $\{\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \cdots, \varepsilon_N\}$

    with $\varepsilon_i = \varepsilon_{\ell i}, \varepsilon_{ui}$

particle i



[+] Can readily be generalized to situations where ε_i takes on many possible values.

$$\therefore Z = \sum_{\text{all } N\text{-particle states } i} e^{-\beta E_i}$$

$$= \underbrace{\sum_{\varepsilon_1 = \varepsilon_{\ell 1}, \varepsilon_{u1}} \sum_{\varepsilon_2 = \varepsilon_{\ell 2}, \varepsilon_{u2}} \cdots \sum_{\varepsilon_N = \varepsilon_{\ell N}, \varepsilon_{uN}}}_{\text{these include all possible strings}} e^{-\beta \overbrace{(\varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_N)}^{\text{Energy of a particular string in the sum}}}$$

[Must understand this step.]

$$= \sum_{\varepsilon_1 = \varepsilon_{\ell 1}, \varepsilon_{u1}} \sum_{\varepsilon_2 = \varepsilon_{\ell 2}, \varepsilon_{u2}} \cdots \sum_{\varepsilon_N = \varepsilon_{\ell N}, \varepsilon_{uN}} e^{-\beta\varepsilon_1} e^{-\beta\varepsilon_2} \cdots e^{-\beta\varepsilon_N}$$

$$= \underbrace{\left(\sum_{\varepsilon_1 = \varepsilon_{\ell 1}, \varepsilon_{u1}} e^{-\beta\varepsilon_1}\right)}_{z_1} \cdot \underbrace{\left(\sum_{\varepsilon_2 = \varepsilon_{\ell 2}, \varepsilon_{u2}} e^{-\beta\varepsilon_2}\right)}_{z_2} \cdots \underbrace{\left(\sum_{\varepsilon_N = \varepsilon_{\ell N}, \varepsilon_{uN}} e^{-\beta\varepsilon_N}\right)}_{z_N}$$

(each sum concerns one particle only)

$$\therefore Z = z_1 \cdot z_2 \cdots z_N$$

(Z is <u>factorized</u>, note "independent" and "distinguishable" play a role)

where

$$z_i = \sum_{\varepsilon_i = \varepsilon_{\ell i}, \varepsilon_{ui}} e^{-\beta\varepsilon_i} = \text{partition function of } i^{\text{th}} \text{ particle}$$

(a single-particle partition function)

easy to evaluate (just sum up 2 terms)

<u>Recall</u>: $F = -kT \ln Z$ (general)

Here $F = -kT \ln(z_1 \cdot z_2 \cdots z_N)$

$$= -kT\ln z_1 - kT \ln z_2 \cdots - kT \ln z_N$$

$$= \underbrace{\sum_{i=1}^{N}}_{\text{sum over particles}} \underbrace{(-kT \ln z_i)}_{i^{th}\text{ particle's contribution (easy to evaluate)}}$$

Then everything follows! Done!

<u>An important observation</u>:

We saw Z factorized! For independent (non-interacting, or weakly interacting that independence is a good approximation) and distinguishable (usually means localized) particles, Z can be factorized into a product of partition functions of each particle.

[Note: For indistinguishable but classical (meaning no need to worry about bosonic/fermionic nature) particles, we need to be more careful about a factor of $\frac{1}{N!}$]

(b) <u>Simple case</u>: Same $\begin{matrix} \text{—}\ \varepsilon_u \\ \text{—}\ \varepsilon_\ell \end{matrix}$ for all particles

$$\begin{array}{ccccc} & 1 & 2 & & N \\ \varepsilon_u & \text{—} & \text{—} & \cdots & \text{—} \\ \varepsilon_\ell & \text{—} & \text{—} & & \text{—} \end{array}$$ } Same single-particle energy states

$$z_1 = z_2 = \cdots = z_N$$

$$\therefore \underbrace{Z}_{\text{partition function of N-particle system}} = z_1^N = \underbrace{z^N}_{\text{partition function of one particle}}$$

where $z = \sum_{\varepsilon = \varepsilon_\ell, \varepsilon_u} e^{-\beta\varepsilon_i} = e^{-\beta\varepsilon_\ell} + e^{-\beta\varepsilon_u}$ (Done!)

- Back to the special case of $\begin{matrix} \varepsilon_u = +\frac{\varepsilon}{2}\ \text{—} \\ \varepsilon_\ell = -\frac{\varepsilon}{2}\ \text{—} \end{matrix}$ $\updownarrow \varepsilon$

$$\boxed{\begin{array}{l} z = \underbrace{e^{\beta\frac{\varepsilon}{2}}}_{\text{from } \varepsilon_\ell = -\frac{\varepsilon}{2} \text{ (bigger)}} + \underbrace{e^{-\beta\frac{\varepsilon}{2}}}_{\text{from } \varepsilon_u = +\frac{\varepsilon}{2} \text{ (smaller)}} = 2\cosh\left(\frac{\beta\varepsilon}{2}\right) \\ \text{and } Z = z^N \end{array}}$$

Think like a physicist!

Physical meaning of the terms in Z

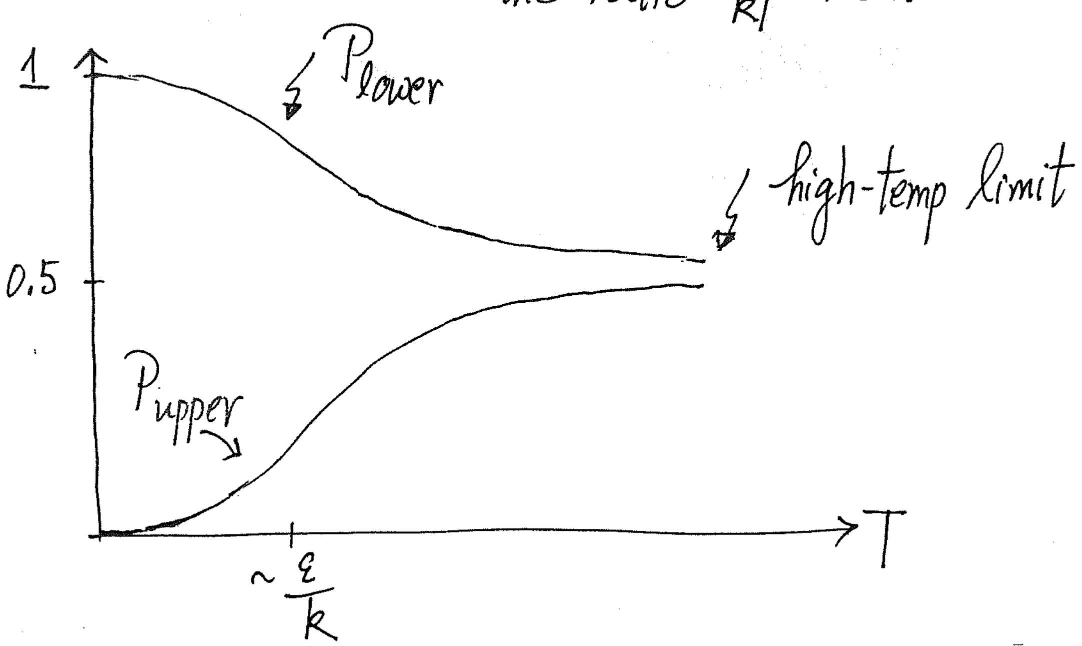
$$Z = \underset{\substack{\uparrow \\ \text{from "lower"} \\ \varepsilon_\ell = -\frac{\varepsilon}{2}}}{e^{\beta\frac{\varepsilon}{2}}} + \underset{\substack{\uparrow \\ \text{from "upper"} \\ \varepsilon_u = +\frac{\varepsilon}{2}}}{e^{-\beta\frac{\varepsilon}{2}}}$$

Recall Z enters as a normalization factor.

$\therefore$ P_{lower} = Probability of a particle occupying the "lower" state of energy $(-\frac{\varepsilon}{2})$ $= \frac{1}{Z} e^{-\beta(-\frac{\varepsilon}{2})} = \frac{1}{Z} e^{\beta\frac{\varepsilon}{2}} = \frac{1}{Z} e^{\frac{\varepsilon}{2kT}}$ (bigger)

P_{upper} = Probability of a particle occupying the "upper" state of energy $(+\frac{\varepsilon}{2})$ $= \frac{1}{Z} e^{-\beta(+\frac{\varepsilon}{2})} = \frac{1}{Z} e^{-\beta\frac{\varepsilon}{2}} = \frac{1}{Z} e^{-\frac{\varepsilon}{2kT}}$ (smaller)

[observe: $\left\{ \begin{array}{l} \varepsilon \text{ competes with } kT \\ \text{the ratio } \frac{\varepsilon}{kT} \text{ matters} \end{array} \right.$]



Ratio of P_{upper} to P_{lower} $= \dfrac{P_{upper}}{P_{lower}} = \dfrac{e^{-\beta\frac{\varepsilon}{2}}}{e^{\beta\frac{\varepsilon}{2}}} = e^{-\beta\varepsilon} = e^{-\frac{\varepsilon}{kT}}$

[Note: ε = $\underbrace{\text{energy difference between the two states}}_{\text{the energy scale in the physical problem}}$]

Low temperature?

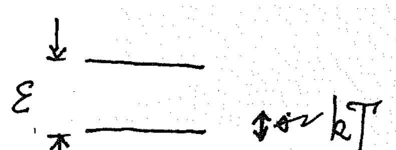
Meaning: $\frac{\varepsilon}{kT} \gg 1$ [See? Need to find an energy in the problem to compare with kT]

$$Z_{low\text{-}temp} = \underbrace{e^{\frac{\varepsilon}{2kT}}}_{\text{very big}} + \underbrace{e^{-\frac{\varepsilon}{2kT}}}_{\text{tiny}} \approx e^{+\frac{\varepsilon}{2kT}}$$

$$P_{lower} = \frac{1}{Z} e^{\frac{\varepsilon}{2kT}} \approx \frac{1}{Z_{low\text{-}temp}} e^{\frac{\varepsilon}{2kT}} \approx 1 \; ; \; P_{upper} \approx 0$$

$$\text{Ratio} = e^{-\frac{\varepsilon}{kT}} \approx 0$$

$\Rightarrow$ All particles are in lower state $(T \to 0)$ and low-temperature physics of the system is dominated by low-energy excitations of the ground state



High temperature?

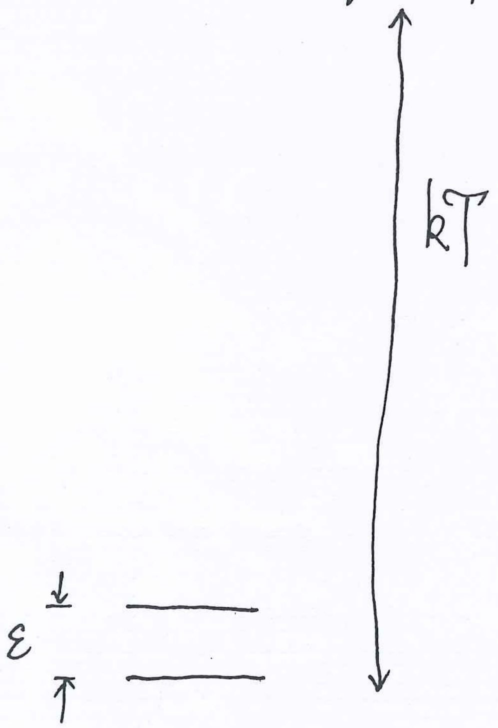
$$\frac{\varepsilon}{kT} \ll 1$$

$$Z_{\text{high-temp}} = \underbrace{e^{\frac{\varepsilon}{2kT}}}_{\approx 1} + \underbrace{e^{-\frac{\varepsilon}{2kT}}}_{\approx 1} \approx 2$$

$$\begin{cases} P_{\text{lower}} = \frac{1}{Z} e^{\frac{\varepsilon}{2kT}} \to \frac{1}{2} \quad \text{(from above)} \\ P_{\text{upper}} = \frac{1}{Z} e^{-\frac{\varepsilon}{2kT}} \to \frac{1}{2} \quad \text{(from below)} \end{cases}$$

Equilibrium physics[+]; can't put more particles in upper state by increasing temperature

{ Two states become equally (almost) occupied at high temperatures



On the scale of kT (big), the two states look almost the same

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[+] To achieve population inversion (e.g. laser), we need some extra effort (pumping) to bring the system out of equilibrium.

Note: These features stem from the bounded nature of the single-particle states, i.e., there is a ceiling in the energy (e.g. two-level, three-level, ..., systems) ⌟

(c) Energy

(i) Physical reasoning:

$$u = \text{average energy per particle}^{+}$$

$$= \frac{1}{Z}\left(\left(\frac{-\epsilon}{2}\right) e^{-\beta\left(-\frac{\epsilon}{2}\right)} + \left(\frac{\epsilon}{2}\right) e^{-\beta\left(\frac{\epsilon}{2}\right)}\right)$$

$$= -\frac{\epsilon}{2Z}\left(e^{\frac{\beta\epsilon}{2}} - e^{-\frac{\beta\epsilon}{2}}\right)$$

$$= \frac{-\epsilon \sinh\frac{\beta\epsilon}{2}}{2\cosh\frac{\beta\epsilon}{2}} = -\frac{\epsilon}{2}\tanh\left(\frac{\beta\epsilon}{2}\right)$$

$\langle E \rangle = N \cdot u$ = average energy of N-particle system in equilibrium at temp. T

$$= -\frac{N\epsilon}{2}\tanh\frac{\beta\epsilon}{2}$$

[+] This is the same as $\langle E \rangle / N$ or U/N.

(ii) Follow calculation scheme:

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = -\frac{1}{Z}\frac{\partial Z}{\partial\beta}$$

$z = 2\cosh\left(\frac{\beta\epsilon}{2}\right)$

$$Z = (z)^N \Rightarrow \ln Z = N\ln z$$

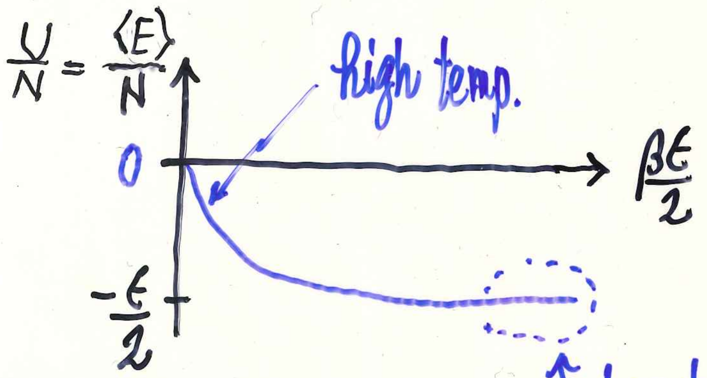
$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = -N\frac{\partial}{\partial\beta}\ln z = -\frac{N}{z}\frac{\partial z}{\partial\beta}$$

$$= -\frac{N}{z}\cdot 2\sinh\left(\frac{\beta\epsilon}{2}\right)\cdot\frac{\epsilon}{2}$$

$$= -\frac{N\epsilon}{z}\sinh\left(\frac{\beta\epsilon}{2}\right)$$

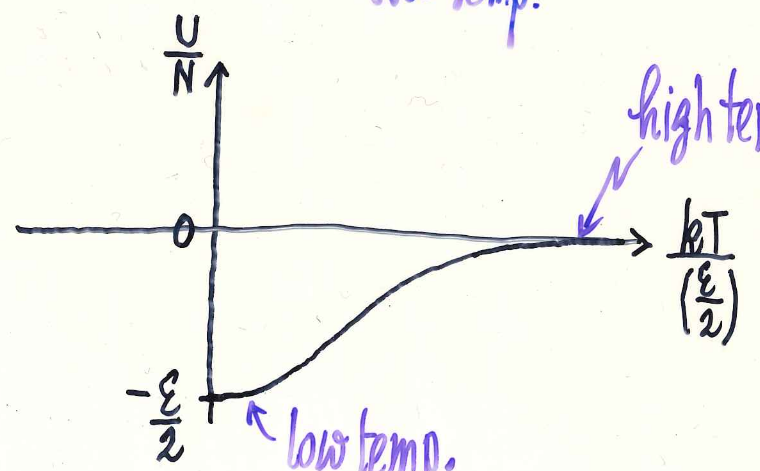
$$= -\frac{N\epsilon}{2}\tanh\left(\frac{\beta\epsilon}{2}\right)$$

(same as before, as it should be)



$\beta \equiv \frac{1}{kT}$

OR



(d) Heat capacity (2-level systems)

$$C = \frac{\partial U}{\partial T}$$

Note: $\beta \equiv \frac{1}{kT}$

$$\boxed{\frac{\partial}{\partial T} = -\frac{1}{kT^2}\frac{\partial}{\partial\beta}}$$

$$C = -\frac{1}{kT^2}\frac{\partial}{\partial\beta}\left(-\frac{N\epsilon}{2}\tanh\frac{\beta\epsilon}{2}\right)$$

$$= \frac{N\epsilon^2}{4kT^2}\operatorname{sech}^2\left(\frac{\beta\epsilon}{2}\right)$$

$$= \underbrace{(Nk)}_{\substack{\sim N \text{ (extensive)} \\ \sim k \text{ (right unit)}}}\underbrace{\left(\frac{\beta\epsilon}{2}\right)^2\operatorname{sech}^2\left(\frac{\beta\epsilon}{2}\right)}_{\text{of the form } x^2\operatorname{sech}^2 x}$$

[behaves as $x^2\operatorname{sech}^2 x$]

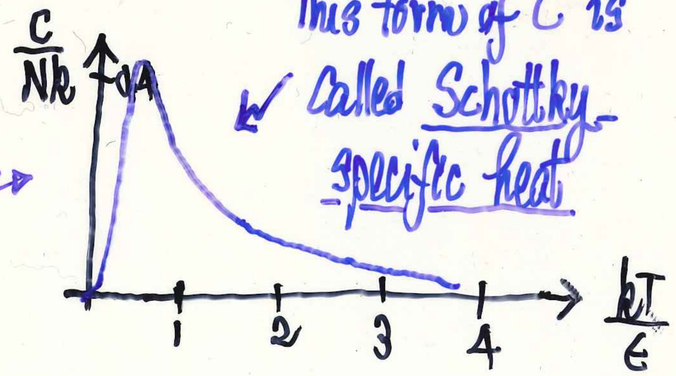
$f(x) = x^2\operatorname{sech}^2 x$ has a maximum at $x = 1.2$ (Ex.)

$\therefore$ C has a peak at $\left(\frac{\beta\epsilon}{2}\right) = 1.2$ or $T = \frac{\epsilon}{2.4k}$

and the peak value is $0.44\,Nk$

- C can also be written as:

$$\boxed{C = Nk(\beta\epsilon)^2\frac{e^{\beta\epsilon}}{(1+e^{\beta\epsilon})^2}}$$



This form of C is called Schottky specific heat

Remark:

- Look at $C = Nk\left(\frac{\varepsilon}{2kT}\right)^2 \operatorname{sech}^2\left(\frac{\varepsilon}{2kT}\right) = Nk\left(\frac{\varepsilon}{kT}\right)^2 \frac{e^{\frac{\varepsilon}{kT}}}{\left(1+e^{\frac{\varepsilon}{kT}}\right)^2}$

  Depends only on the ratio $\frac{\varepsilon}{kT}$, but not ε alone and kT alone!

- Universal behavior

  details of problems do not matter!

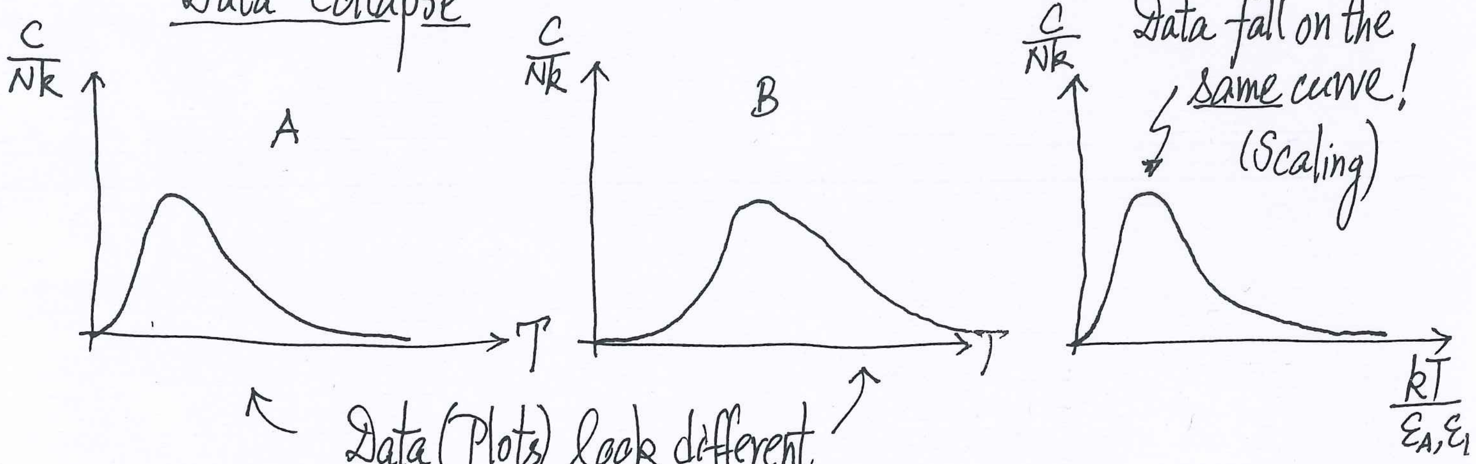
  e.g. Problem A [a kind of defect] vs Problem B

  ε_A = excitation energy $\qquad$ ε_B = excitation energy

Physics of Problem A at a temperature $T = \frac{\varepsilon_A}{\mathcal{A}k}$	is the same as	Physics of Problem B at a temperature $T' = \frac{\varepsilon_B}{\mathcal{A}k}$

($\mathcal{A}$ = a constant)

Data Collapse



(e) Free Energy

$$F = -kT\ln Z = -\overset{\text{extensive}}{N}kT\ln z$$

$$= -NkT\ln\underbrace{\left(2\cosh\frac{\beta\varepsilon}{2}\right)}_{z}$$

$$S = -\frac{\partial F}{\partial T}$$

$$= Nk\ln z + \frac{NkT}{z}\frac{\partial z}{\partial T}$$

$$= Nk\ln z - \frac{NkT}{zkT^2}\frac{\partial z}{\partial \beta}$$

$$= Nk\ln z - \frac{N\varepsilon}{zT}\sinh\frac{\beta\varepsilon}{2}$$

$$= Nk\ln z - \frac{2Nk}{z}\left(\frac{\beta\varepsilon}{2}\right)\sinh\frac{\beta\varepsilon}{2}$$

and other quantities can be calculated.

Check: High-temperature behavior

$\beta \to 0$, $\quad S = Nk\ln 2 \quad$ (Why? physical sense)

One-page Summary on two-level systems: Canonical Ensemble

Collection of N "two-level" particles

- Independent & distinguishable

$$Z = \prod_{i=1}^{N} z_i \; ; \; z_i = \text{single-particle partition function}$$

$$= \sum_{\varepsilon_i = \varepsilon_{\ell,i}, \varepsilon_{u,i}} e^{-\beta \varepsilon_i}$$

i^{th} particle

$$= e^{-\beta \varepsilon_{\ell,i}} + e^{-\beta \varepsilon_{u,i}}$$

$\varepsilon_{u,i}$ — upper
$\varepsilon_{\ell,i}$ — lower

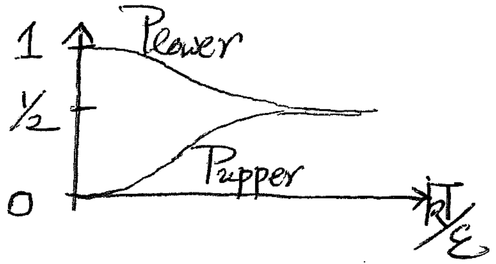
- Same — $+\varepsilon/2$, — $-\varepsilon/2$ for all particles

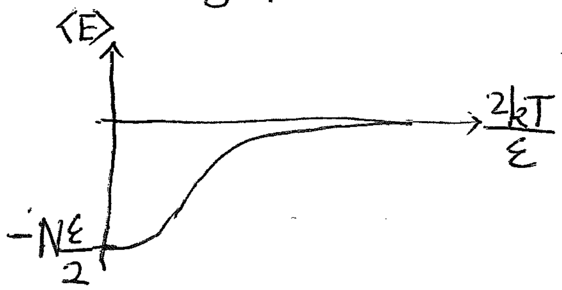
$$Z = z^N \; ; \; z = e^{\beta\varepsilon/2} + e^{-\beta\varepsilon/2} = 2\cosh\left(\frac{\beta\varepsilon}{2}\right)$$

$$\begin{cases} P_{lower} = \frac{1}{z} e^{\beta\varepsilon/2} = \text{Prob. of finding a particle in lower state} \\ P_{upper} = \frac{1}{z} e^{-\beta\varepsilon/2} = \text{Prob. of finding a particle in upper state} \end{cases}$$

- $\langle E \rangle = -\frac{\partial}{\partial\beta} \ln Z$ (or by physical reasoning)

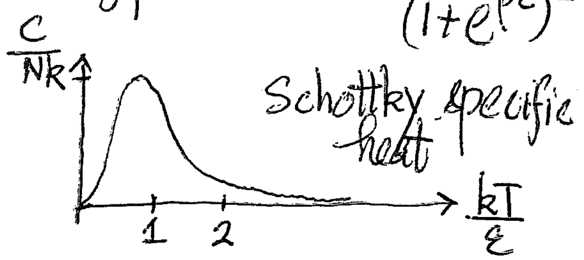
$$= -N \frac{\varepsilon}{2} \tanh\left(\frac{\beta\varepsilon}{2}\right)$$





- Heat capacity

$$C = \frac{\partial \langle E \rangle}{\partial T} = Nk (\beta\varepsilon)^2 \frac{e^{\beta\varepsilon}}{(1+e^{\beta\varepsilon})^2}$$



- Entropy $S = \frac{\langle E \rangle - F}{T}$ or $S = -\frac{\partial F}{\partial T}$

$$S = Nk \ln z - \frac{2Nk}{z}\left(\frac{\beta\varepsilon}{2}\right) \sinh\left(\frac{\beta\varepsilon}{2}\right)$$

Remarks

- For comparison, the following pages give the microcanonical ensemble approach of the two-level systems. We have worked the problem out, e.g. Schottky defects problem.

A'. Two-level systems (microcanonical Ensemble)

This is the same problem, but here it is treated within the microcanonical ensemble.

- N distinguishable, non-interacting particles
- each particle can be in either $\epsilon_l = -\frac{\epsilon}{2}$ or $\epsilon_u = \frac{\epsilon}{2}$

[Note: In microcanonical ensemble, the temperature T is a quantity that we derive.]

Let E = total energy (we specify (E,N,V) in microcanonical ensemble)

Let $E = M\left(\frac{\epsilon}{2}\right)$

where M can be $-N, -N+2, -N+4, \ldots, N-2, N$

Question: Discuss the thermodynamic properties of the system for the range of energy $E<0$

For a value of M (i.e., fixed E but $E<0$), [macrostate]

let n_+ = # particles with energy $\frac{+\epsilon}{2}$

n_- = # particles with energy $\frac{-\epsilon}{2}$

of course $\boxed{n_+ + n_- = N}$ — ①

then $E = n_+\left(\frac{\epsilon}{2}\right) + n_-\left(\frac{-\epsilon}{2}\right) = (n_+ - n_-)\left(\frac{\epsilon}{2}\right)$

$\therefore \boxed{M = n_+ - n_-}$ — ②

From ① and ②, we can express n_+ and n_- in terms of N and M (this is E)

$$n_+ = \frac{1}{2}(N+M) \; ; \quad n_- = \frac{1}{2}(N-M)$$

- The microcanonical ensemble has to do with counting the number of microstates $W(E,N,V)$ or $W(M,N,V)$, $E = M\left(\frac{\epsilon}{2}\right)$

$$W(M,N,V) = \frac{N!}{n_+!\, n_-!} = \frac{N!}{\left(\frac{1}{2}(N+M)\right)!\left(\frac{1}{2}(N-M)\right)!}$$

(N objects into two groups: n_+ in one group, n_- in another group)

- $S = k \ln W$

$$= k\left[\ln N! - \ln n_+! - \ln n_-!\right]$$

$$= k\left[N\ln N - \cancel{N} - n_+ \ln n_+ + \cancel{n_+} - n_- \ln n_- + \cancel{n_-}\right] \quad \text{Stirling's formula}$$

$$= k\left[(n_+ + n_-)\ln N - n_+ \ln n_+ - n_- \ln n_-\right]$$

$$= -k\left[n_- \ln\frac{n_-}{N} + n_+ \ln\frac{n_+}{N}\right] \quad \text{— ③}$$

$$= -Nk\left[\frac{n_-}{N}\ln\frac{n_-}{N} + \frac{n_+}{N}\ln\frac{n_+}{N}\right]$$

← You may be able to write down this result directly

$$= k\left[N\ln N - \left(\frac{N+M}{2}\right)\ln\frac{N+M}{2} - \left(\frac{N-M}{2}\right)\ln\left(\frac{N-M}{2}\right)\right] \quad \text{— ④}$$

← shows explicitly that $S(E)$ or $S(M)$

It will be interesting to see how S depends on E (or M since $E = M\left(\frac{\varepsilon}{2}\right)$)

Let's think:

- Lowest possible energy $E_{min} = -N\left(\frac{\varepsilon}{2}\right)$

  physical situation: every particle in low energy state

  number of microstate $= 1$

  $\ln W = 0$ (entropy $= 0$)

- "Highest" possible energy† $= +N\left(\frac{\varepsilon}{2}\right)$

  physical situation: every particle in high energy state

  number of microstate $= 1$

  $\ln$(number of microstate) $= 0$

- When half of particles in low energy state and half in high energy state

  $\Rightarrow$ largest number of microstates

  $\Rightarrow$ $\underbrace{\text{largest entropy}}$ ← should correspond to $T \to \infty$

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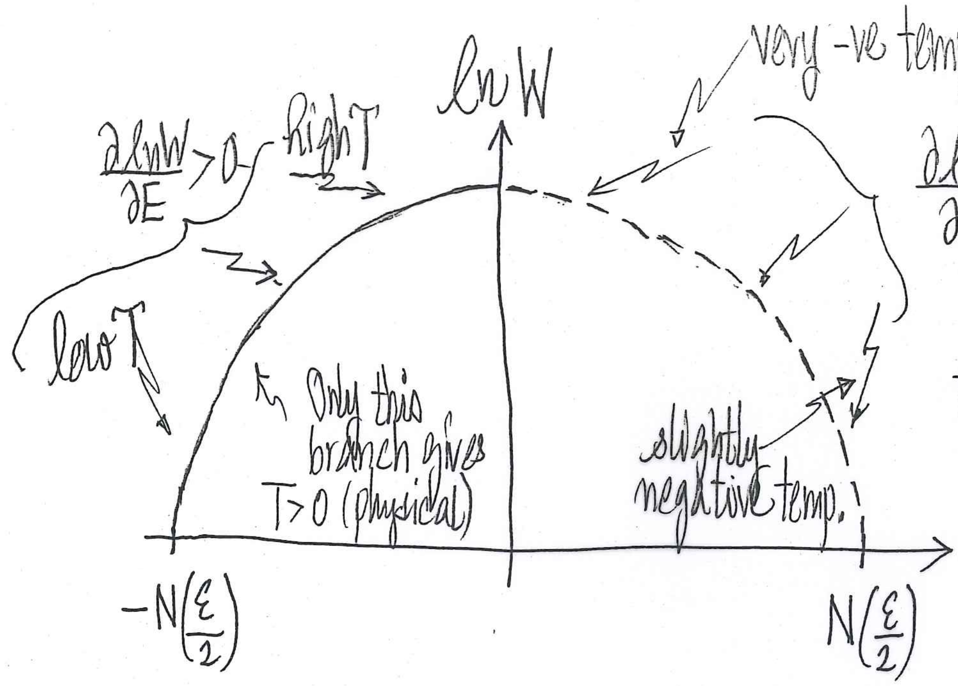
† This cannot be achieved by increasing the temperature.

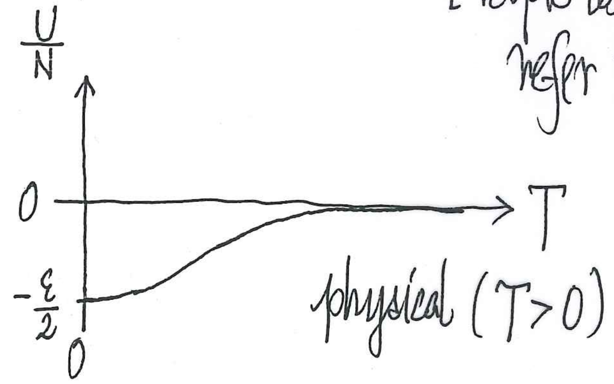


If we insist on talking about "temperature", then this branch has negative temperatures

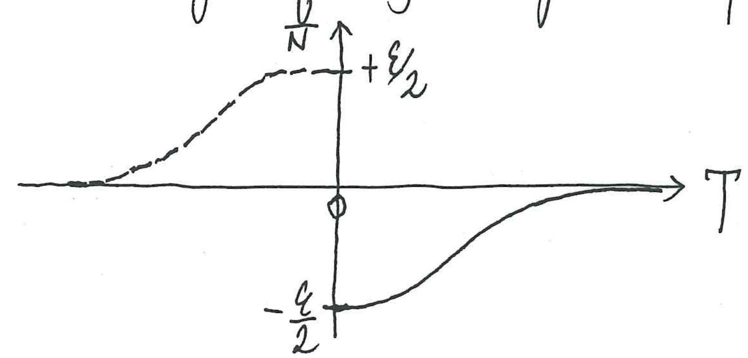
Recall: $\frac{1}{T} = \underbrace{\frac{\partial S}{\partial E}}_{\text{slope of curve}}$ Physically: $T > 0$

For $E > 0$, $\frac{\partial \ln W}{\partial E} < 0 \Rightarrow$ this branch can't be reached by physical temperatures.

[People use "negative temperatures" to refer to situations like this]



If we insist on plotting U even for negative temperatures:



• Eqs (3) and (4) for S don't look like our result

$$S = Nk \ln z - \frac{2Nk}{z}\left(\frac{\beta\epsilon}{2}\right)\sinh\left(\frac{\beta\epsilon}{2}\right)$$

[But, wait and see!]

• Temperature T: [T is derived in microcanonical ensemble]

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{1}{\left(\frac{\epsilon}{2}\right)}\frac{\partial S}{\partial M} \qquad \text{(using (4) will be convenient)}$$

$$= \frac{k}{\epsilon}\ln\left(\frac{N-M}{N+M}\right) \qquad (5)$$

[Note: If $M>0$ (thus $E>0$), then $T<0$, the system is not normal in the sense of stat. mech. (people call this negative temperature).
This is why we restrict ourselves to consider $E<0$ ($M<0$) only.]

• Note:

$$\frac{n_-}{n_+} = \frac{N-M}{N+M}$$

$$\therefore \frac{1}{T} = \frac{k}{\epsilon}\ln\frac{n_-}{n_+} \Rightarrow \frac{n_-}{n_+} = e^{\epsilon/kT}$$

$$\text{OR } \frac{n_-}{n_+} = e^{-\epsilon/kT}$$

Also,

$$\frac{n_+}{N} = \frac{n_+}{n_+ + n_-} = \frac{1}{1+\frac{n_-}{n_+}} = \frac{1}{1+e^{\epsilon/kT}} = \frac{e^{-\epsilon/2kT}}{e^{-\frac{\epsilon}{2kT}} + e^{\epsilon/2kT}} = \frac{1}{z}e^{-\epsilon/2kT} \qquad (6)$$

(same result obtained by canonical ensemble)

Similarly, we can show

$$\frac{n_-}{N} = \frac{e^{\frac{\epsilon}{2kT}}}{e^{\frac{\epsilon}{2kT}} + e^{-\frac{\epsilon}{2kT}}} = \frac{1}{z}e^{\frac{\epsilon}{2kT}} \qquad (7)$$

$$E = M\left(\frac{\epsilon}{2}\right) = -(n_- - n_+)\left(\frac{\epsilon}{2}\right)$$

$$= -N\left[\frac{e^{\frac{\epsilon}{2kT}} - e^{-\frac{\epsilon}{2kT}}}{e^{\frac{\epsilon}{2kT}} + e^{-\frac{\epsilon}{2kT}}}\right]\left(\frac{\epsilon}{2}\right)$$

$$\Rightarrow E = -N\left(\frac{\epsilon}{2}\right)\tanh\left(\frac{\epsilon}{2kT}\right) \# \qquad (8)$$

(Same result as obtained by canonical ensemble)

$$C = \frac{dE}{dT} = Nk\left(\frac{\epsilon}{2kT}\right)^2 \operatorname{sech}^2\left(\frac{\epsilon}{2kT}\right) \# \qquad (9)$$

(same as before)

$$\text{Using } S = -kN\left[\frac{n_-}{N}\ln\frac{n_-}{N} + \frac{n_+}{N}\ln\frac{n_+}{N}\right] \qquad \text{(Eq. (3))}$$

$$= -kN\left[\frac{e^{\frac{\epsilon}{2kT}}}{z}\ln\frac{e^{\frac{\epsilon}{2kT}}}{z} + \frac{e^{-\frac{\epsilon}{2kT}}}{z}\ln\frac{e^{-\frac{\epsilon}{2kT}}}{z}\right] \qquad \text{(using Eq. (6), (7))}$$

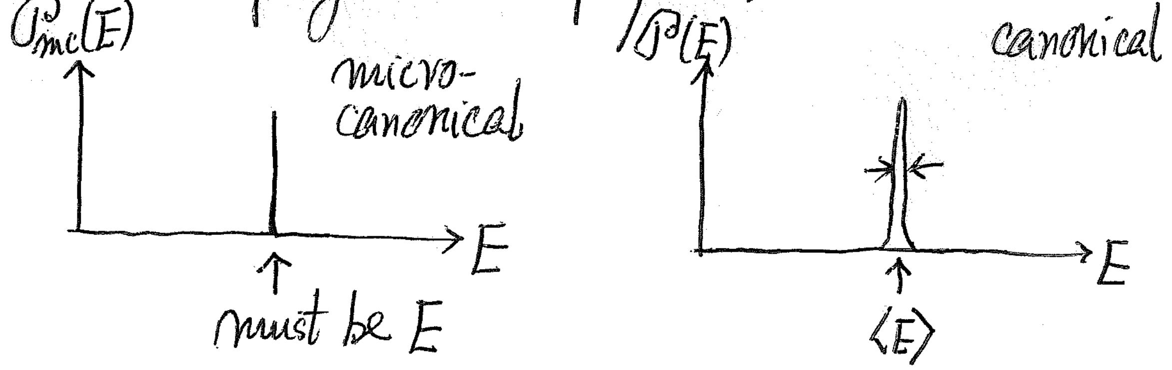
$$= -\frac{kN}{z}\left[e^{\frac{\epsilon}{2kT}}\left(\frac{\epsilon}{2kT} - \ln z\right) + e^{-\frac{\epsilon}{2kT}}\left(\frac{-\epsilon}{2kT} - \ln z\right)\right]$$

$$= \frac{Nk}{z}\left[\ln z\left(e^{\frac{\epsilon}{2kT}} + e^{-\frac{\epsilon}{2kT}}\right) - \frac{\epsilon}{2kT}\left(e^{\frac{\epsilon}{2kT}} - e^{-\frac{\epsilon}{2kT}}\right)\right]$$

$$= Nk\ln z - \frac{Nk}{z}\left(\frac{\epsilon}{2kT}\right) 2\sinh\left(\frac{\epsilon}{2kT}\right) \qquad (10)$$

which is the same result as obtained in the canonical ensemble approach.

- Now, you have seen the same problem solved in two methods.
- Of course, the same physics comes out! (∵ physics is physics!)



But for macroscopic systems, $\langle E\rangle$ is very sharp!

- You can decide which method is more convenient.